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X-RAY STUDIES OF POLYBUTENE-1, POLYPENTENE-1 AND POLYHEXENE-1

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ABSTRACT

The effect of mechanical and thermal treatment on the x-ray diffraction patterns of polybutene-1, polypentene-1, and polyhexene-1 is examined. These variables are found to influence the transformation among polymorphic forms of these polymers.

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THEORY

Polybutene-1 is known to have two crystalline structures, one stable and the other unstable. The first extensive study of this polymer was carried out by Natta's group.[1,2] In his paper the stable and unstable structures were named the modification 1 and the modification 2, respectively. Transformation from the unstable to stable form is effected by the following processes: (1) aging, (2) pressure, (3) temperature, and (4) mechanical stretching.

The crystalline structure of polybutene-1 was studied by Natta's group [2] especially with respect to the stable form. The structure of the unstable form was investigated by Miller.[3] The variation between the two structures, according to the crystallographic data by Miller,[3] is indicated in the table below.

	Crystal System	Space Group	Unit Cell in Angstroms			Monomer Units in Cell
			a_0	b_0	c_0	
Modification 1	Rho	$D_{3d} - R\bar{3}c$	17.7	17.7	6.50	18
Modification 2	Tet		7.49	7.49	6.85	

The various properties of modification 1 (the stable form) are listed as follows:

Density g./cm^3		M.P. oC.	Heat of Fusion k cal/ monomer unit	Chain Conformation
Cryst.	Amorph.			
0.95	0.87	126	3.33	3 – 1

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The crystalline structure of the stable form polybutene-1 is illustrated in Fig. 1, and the assignment of the x-ray reflection pattern to individual peaks is given in Fig. 2.

Recently a quantitative study of the transformation from the unstable to the stable form was conducted by Zannetti, Manaresi and Buzzoni.[4] They studied the behaviour of polybutene-1 subjected to temperature, pressure and aging effects by using an x-ray diffraction method, and proposed a method for determination of crystallinity.

Very little study has been made with respect to polypentene-1. The complete analysis of crystalline structure has not been published,[3] and only fragmentary data available from Miller's crystallographic data are listed as follows:

Unit Cell Parameters			M.P.	Chain Conformation
a_0	b_0	c_0 α, β, γ	°C.	
6.60	0.96		75	4 – 1

Since the assignment of the peaks of the x-ray diffraction pattern is not available, the extension of the orientation study which has been conducted so far with lower homologs of polyolefins such as polyethylene, polypropylene and polybutene-1, was not carried out in this case.

Polyhexene-1 [3] takes the viscous liquid state at room temperature because its melting point is so low (– 55°C.). This is a very peculiar feature when compared with lower homologous poly-α-monoolefins. The same low melting behaviour is encountered in the cases of polyheptene-1 (m.p. –40°C.) and polyoctene-1 (m.p. –38°C.) .[3] The melting point then goes up with polydodecene-1 (m.p. 45°C.) and with polyoctadecene-1 (m.p. 80°C.).[3] This variation of melting behaviour is supposed to be caused by the variation of the structures of various polyolefins.

EXPERIMENTAL

(1) Polybutene-1

Transformation of the crystalline structure of polybutene-1 was studied by the techniques of x-ray diffraction, birefringence and optical microscopy. Among these methods, x-ray diffraction was the only method found applicable for the pursuit of the transformation. Photomicroscopic study of polybutene-1 spherulites has been presented previously.[5] It is rather difficult to find any trace of a structural change on account of the aging effect in these photomicrographs. This transformation is also too subtle to be detected by birefringence changes as measured with a Babinet compensator. Hence, the application of x-ray diffraction method to the modification of polybutene-1 will be presented here.

In our study, the aging and mechanical effects on the transformation of polybutene-1 were examined by means of x-ray radial Geiger scan and by x-ray photograph. The other aspect was the determination of amorphous peak of polybutene-1, if such an amorphous peak analogous to those in polyethylene and polypropylene exists. For this purpose an x-ray radial scan of the molten sample was carried out.

The samples were prepared in quenched or annealed form, as mentioned previously,[6] and investigated either immediately after the preparation (Fresh sample) or after aging at room temperature for a given time (Aged sample). Mechanical stretching devices (manual stretching apparatus and Instron Tensile Tester) were used to orient the sample.

In the case of both the annealed and quenched polybutene-1 film, the sheet of the specimen was cut into four pieces in order to measure the radial scan of:

(1) Fresh sample, unoriented

(2) Fresh sample, oriented

(3) Aged sample, unoriented

(4) Aged sample, oriented.

The thickness of the samples ranged from 5 to 10 mils. The samples were clamped in the brass rings,[6] especially devised for the x-ray and other optical study of polymer films,either without any orientation or after stretching the sample to a given elongation ratio.

The x-ray radial scan was made using the same apparatus as previously described. For the correction of the observed x-ray intensity, the IBM 1620 program [6] introduced previously was utilized extensively.

Films of polybutene-1 subjected to various ratios of elongation were studied by x-ray photographs. The voltage and current of the x-ray source were 40 kv. and 20 ma., respectively. A Ni filter was used to obtain CuKα incident x-ray beam. The distance between the sample and x-ray film plate (Kodak No Screen) was 5 cm., and the exposure time varied in general between 3 and 4 hours. The film exposed to x-ray was processed by Kodak x-ray developer and fixer.

The thickness of the sample was 5 to 10 mils, depending upon the extent of elongation. All the samples were mounted in the brass rings, and the direction of the orientation was aligned in the longitudinal direction of the film. The samples were oriented by using the manual stretching instrument which was devised in this laboratory.

The determination of the amorphous peak of polybutene-1 was substantiated by making the radial scan in molten state of polybutene-1 at 150° C., about 20°C. higher than the melting point of polybutene-1 (131°C.), together with the scans at room temperature before and after the melting.

For this purpose, a considerably thicker sample (ca 30 mils) was mounted in the brass ring with the mica windows on each side. The oven in which the sample was mounted was heated by circulating air over electrical heaters. The temperature of the oven was regulated within $\pm$ 2° C. by a thermister controller.

(2) Polypentene–1

Since no assignment of the x-ray diffraction peaks of polypentene–1 has been published, a detailed analysis of orientation effects in terms of an orientation function formulation was not carried out. The effects of heat treatment and orientation were studied by x-ray Geiger counter radial scan and by x-ray photographs, as was done in the case of polybutene–1. Preparation of the sample was carried out in the same way as with polybutene–1 except that the sample was melted in the Carver Laboratory Press at a lower temperature (95°C.).

The correction of x-ray radial scan data was not made as no further extension of this study is practicable at the present stage with the lack of structural details. Polypentene–1 annealed and quenched films with various elongation ratios were investigated by x-ray photographs to check the variation of the structure by heat treatment and sample orientation, and to ascertain whether or not polymorphic phenomena analogous to that of polybutene–1 are present in polypentene–1.

(3) Polyhexene–1

The viscous, liquid state polyhexene–1 was pressed into film between two sheets of cellophane in the Carver Press at room temperature. After peeling off the cellophane by immersion of the sample in water, the sample was mounted into the brass ring to take the x-ray picture. No study of polyhexene–1 at temperatures lower than room temperature was carried out.

RESULTS AND DISCUSSION

In Figs. 3 and 4, the x-ray radial scan diagrams of polybutene–1 quenched film oriented to various stages are plotted against the Bragg angle (2θ) in order to clarify the modification of crystalline structures obtained either by aging or by mechanical stretching.

In Fig. 3 the unstable structure found in the fresh sample is observed to be converted into the stable structure by orientation. After 150% elongation of the fresh sample, the stable form completely takes the place of the unstable form. In Fig. 4, the unstable form which still remains after aging for 7 days at room temperature is seen to vanish completely as the sample is stretched to 190%. The effect on the modification by aging at higher temperatures was not ascertained. From these figures, one can see clearly that the unstable structure which dominates just after the preparation of the film develops into the stable form, as the sample is either aged or oriented, and that meanwhile the structure of polybutene–1 film is characterized by the coexistence of two modifications.

The same sort of mechanical and time effects are also observed in the case of the polybutene–1 annealed sample. When viewed under the polarized microscope, the annealed sample is seen to be more spherulitic than the quenched one, and hence more brittle. It was difficult to stretch the sample more than

60%, even by employing the slowest speed of an Instron Tensile Tester. From Fig. 5, the unstable structure is obviously observed to have disappeared after 60% elongation of the fresh sample. A very small peak at $2\theta \approx 11.6^{\circ}$ is still observable, but the peak at $2\theta \approx 16.7^{\circ}$ is completely degenerated. The aging effect is also very remarkable. In Fig. 6, allowing the unoriented sample to remain for 8 days at room temperature results in a complete transformation to the stable form. When the aged sample is oriented, the contribution from the unstable form is no longer detectable.

Fig. 7 shows the x-ray photographs of polybutene-1 quenched film at various stages of orientation. The modification of the structure of polybutene-1 discussed above on the basis of the x-ray radial scan arises in these pictures as well. Two modifications, stable and unstable, observed in the picture of the fresh unoriented sample, turn into a single stable structure as the sample is aged or stretched mechanically. At the highest elongation achieved (200% in this case), a fairly well-developed fiber diagram is obtained.

The same study was carried out for polybutene-1 annealed film, but in this case the sample was too hard and brittle to allow orientation higher than 50% to be achieved. One can observe little change of the x-ray reflection rings as the sample is oriented to 50% elongation ratio in Fig. 8. The shift of the structure from unstable to stable was also seen in this case.

The result of melting on an x-ray radial scan of polybutene-1 is illustrated in Fig. 9. The sample examined was an unoriented aged sample. After making the radial scan of this original sample, the temperature of the oven was elevated up to 150°C.. The radial scan of the molten sample at this temperature took such shape of the curve as shown in Fig. 9 . Two broad peaks are obtained. This result agrees with that of the Italian group, [4] although the position of the second peak seems to deviate a little from their results. The fact that there are two peaks in the x-ray diagram of the amorphous state of polybutene-1 is very interesting when one compares this with polyethylene and polypropylene to which only one amorphous peak is assigned. Once the position of the amorphous peak is known, it may be possible to obtain the degree of crystallinity by Hermans' method [7] (which was discussed previously), provided that the construction of the amorphous peak can be done properly. The Italian group has tried to measure the crystallinity by comparing the crystalline and amorphous peak, but the reliability seems still somewhat dubious.

After the radial scan of the molten sample was finished, the oven was allowed to cool down to room temperature by shutting off the heating system. When room temperature was reached, the radial scan was repeated and this indicated that the same unstable structure as was seen before predominates immediately after the formation of the film.

As mentioned previously, the assignment of the x-ray diffraction peaks of polypentene-1 is not available. Therefore, the interpretation of the x-ray work concerned with this polymer is rather limited. However, the results are given here in behalf of future study.

In Fig. 10, x-ray photographs of annealed polypentene–1 are shown at various elongation ratios. The same kind of study was extended to quenched polypentene–1 film in Fig. 11. Fairly complex patterns are exhibited in both of them. (At higher elongation, the sample is seen to give the fiber diagram.) The results of the x-ray radial scan without correction are shown in Fig. 12. From these results, in the case of polypentene–1, as far as the x-ray study is concerned there is no sign of the existence of various modifications such as have been encountered with polybutene–1; at least, on the time scale used in this study.

With respect to polyhexene–1, which is liquid at room temperature, the x-ray photograph (Fig. 13) shows only a smeared type ring characteristic of amorphous order in the material.

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CAPTIONS FOR FIGURES

Figure 1 Conformation of polybutene-1 in the crystalline state.

Figure 2 Assignment of the x-ray diffraction diagram of polybutene-1

Figure 3 X-ray radial scan of quenched polybutene-1 fresh sample.

Figure 4 X-ray radial scan of quenched polybutene-1 aged sample

Figure 5 X-ray radial scan of annealed polybutene-1 fresh sample

Figure 6 X-ray radial scan of annealed polybutene-1 aged sample

Figure 7 X-ray diffraction photographs of quenched polybutene-1 at various percentages of elongation

Figure 8 X-ray diffraction photographs of annealed polybutene-1 unoriented and oriented

Figure 9 Plot of x-ray diffraction intensity as a function of temperature in radial scans of annealed polybutene-1

Figure 10 X-ray diffraction photographs of annealed polypentene-1 at various percentages of elongation

Figure 11 X-ray diffraction photographs of quenched polypentene-1 at various percentages of elongation

Figure 12 X-ray radial scan of quenched and annealed polypentene-1

Figure 13 X-ray diffraction photograph of polyhexene-1

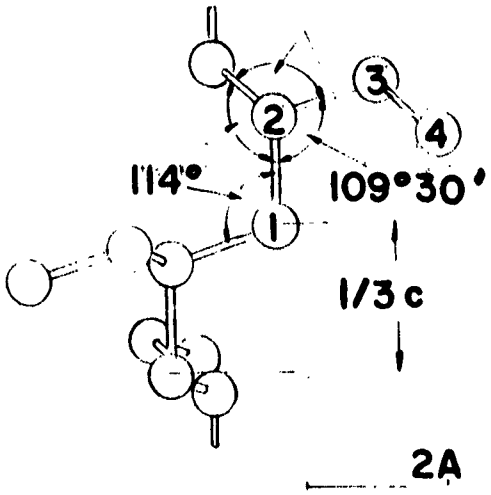

FIG.1-1 [2)] MODEL OF THE STRUCTURAL UNIT OF POLYBUTENE-1 (C-C = 1.54 A)

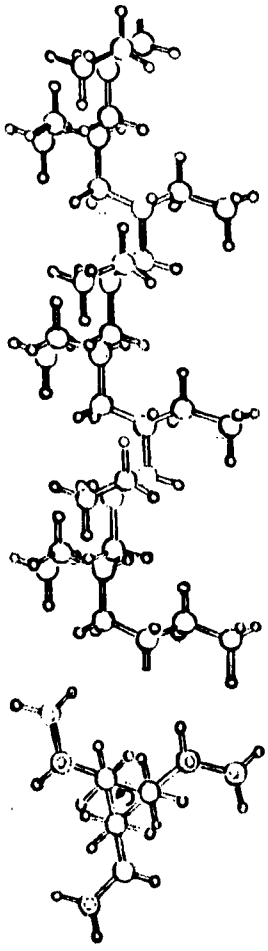

FIG.1-2 POLYBUTENE-1 STABLE FORM CRYSTALLINE STATE

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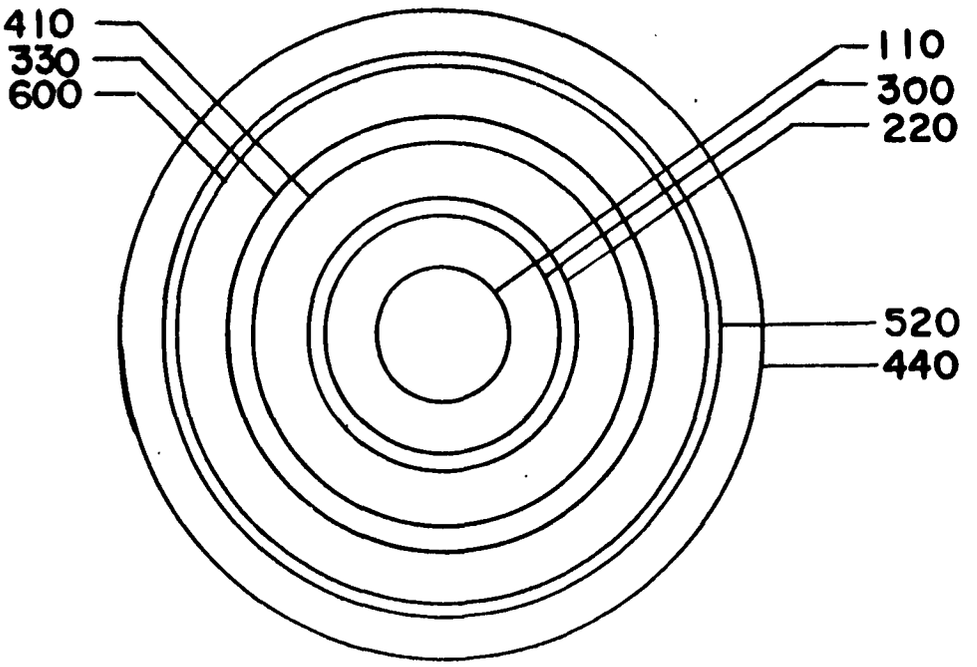

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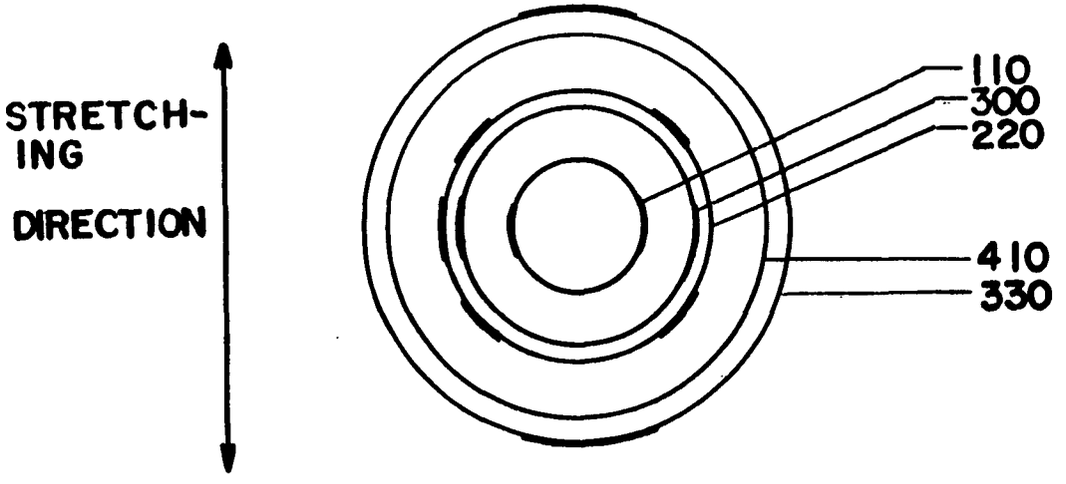


POLYBUTENE-I STABLE FORM

MILLER INDICES

FIG. 2

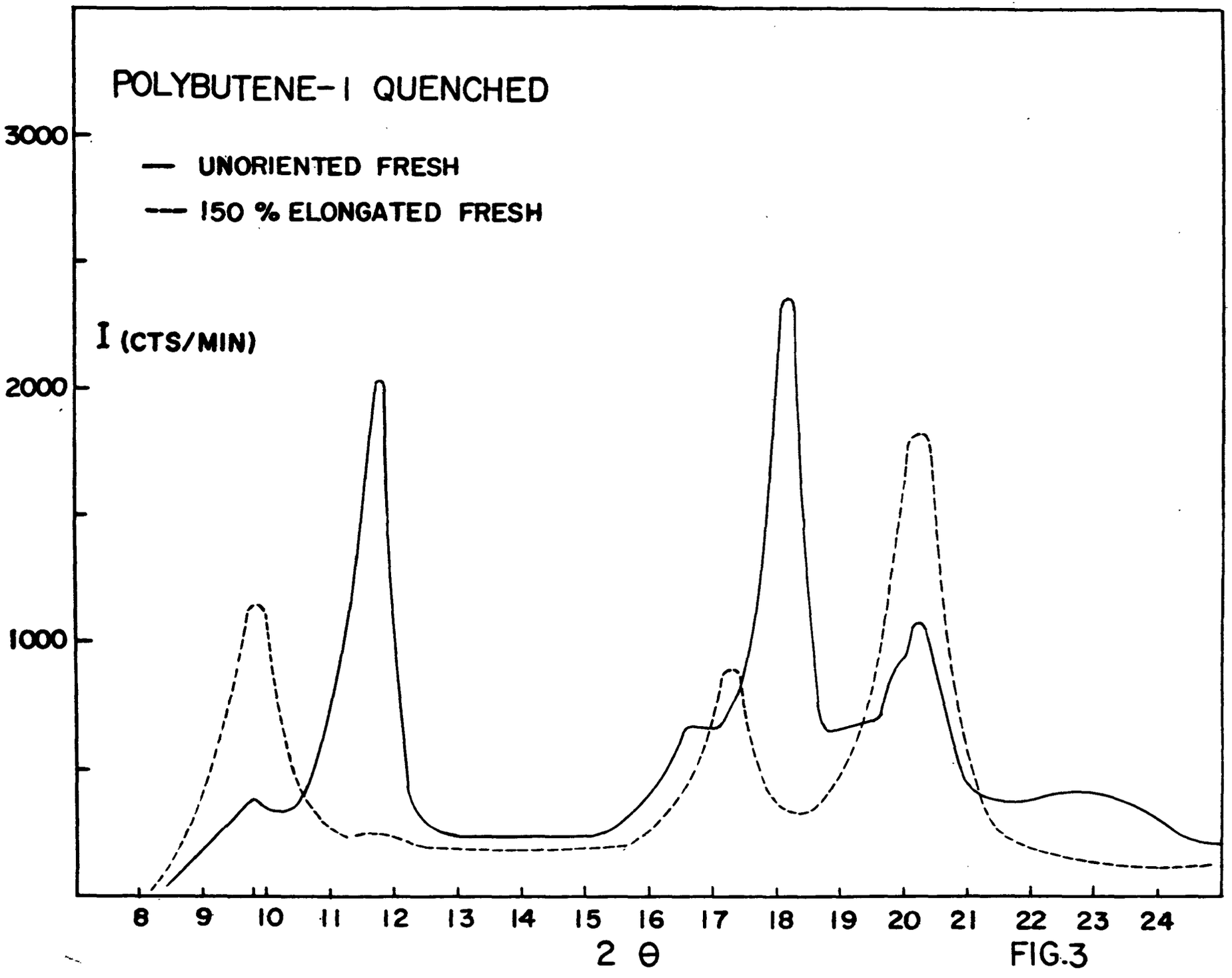

POLYBUTENE-1 QUENCHED
— UNORIENTED FRESH
--- 150 % ELONGATED FRESH
I (CTS/MIN)
3000
2000
1000
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
2 θ

FIG.3

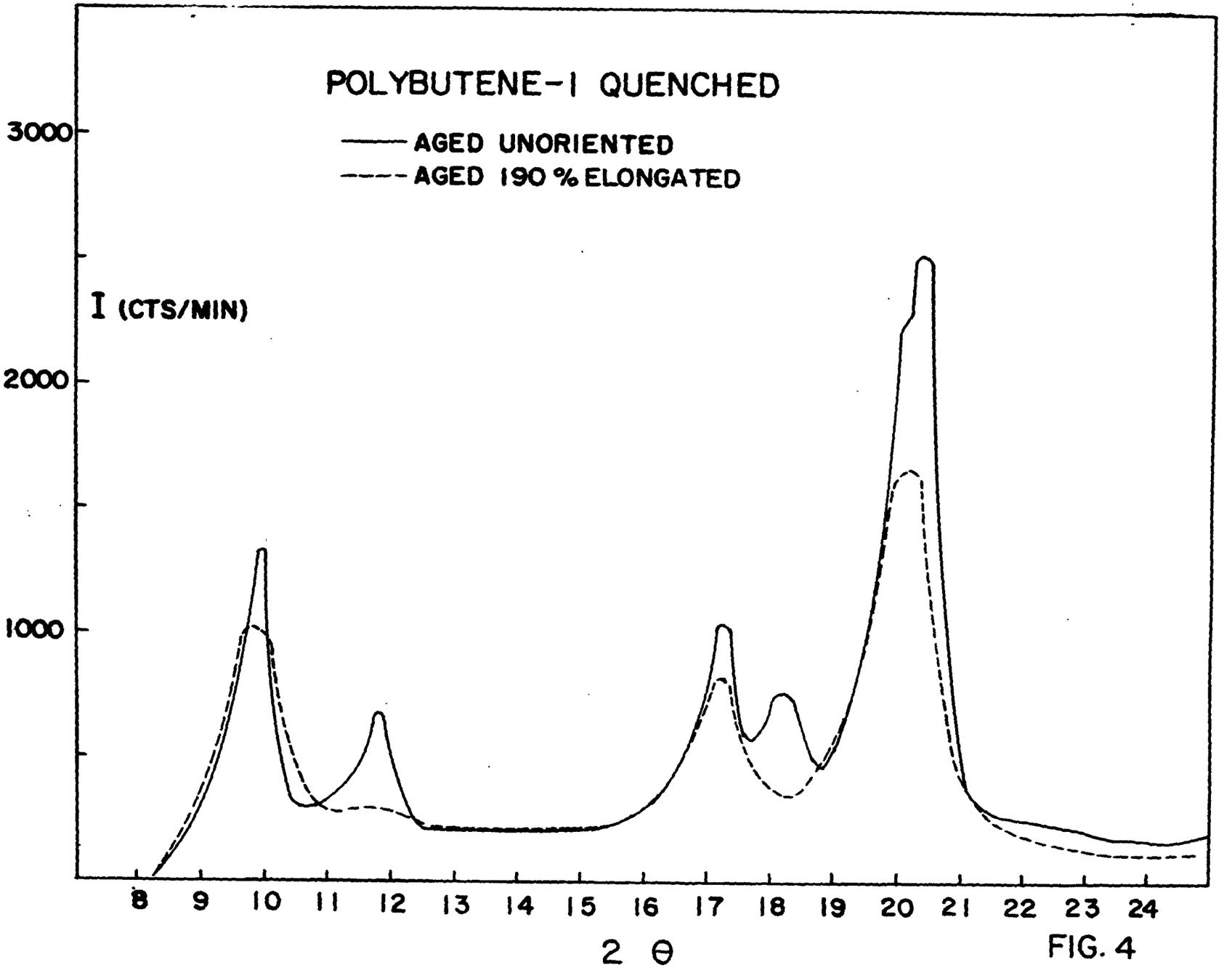

POLYBUTENE-1 QUENCHED
AGED UNORIENTED
AGED 190 % ELONGATED
I (CTS/MIN)
3000
2000
1000
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
2 θ

FIG. 4

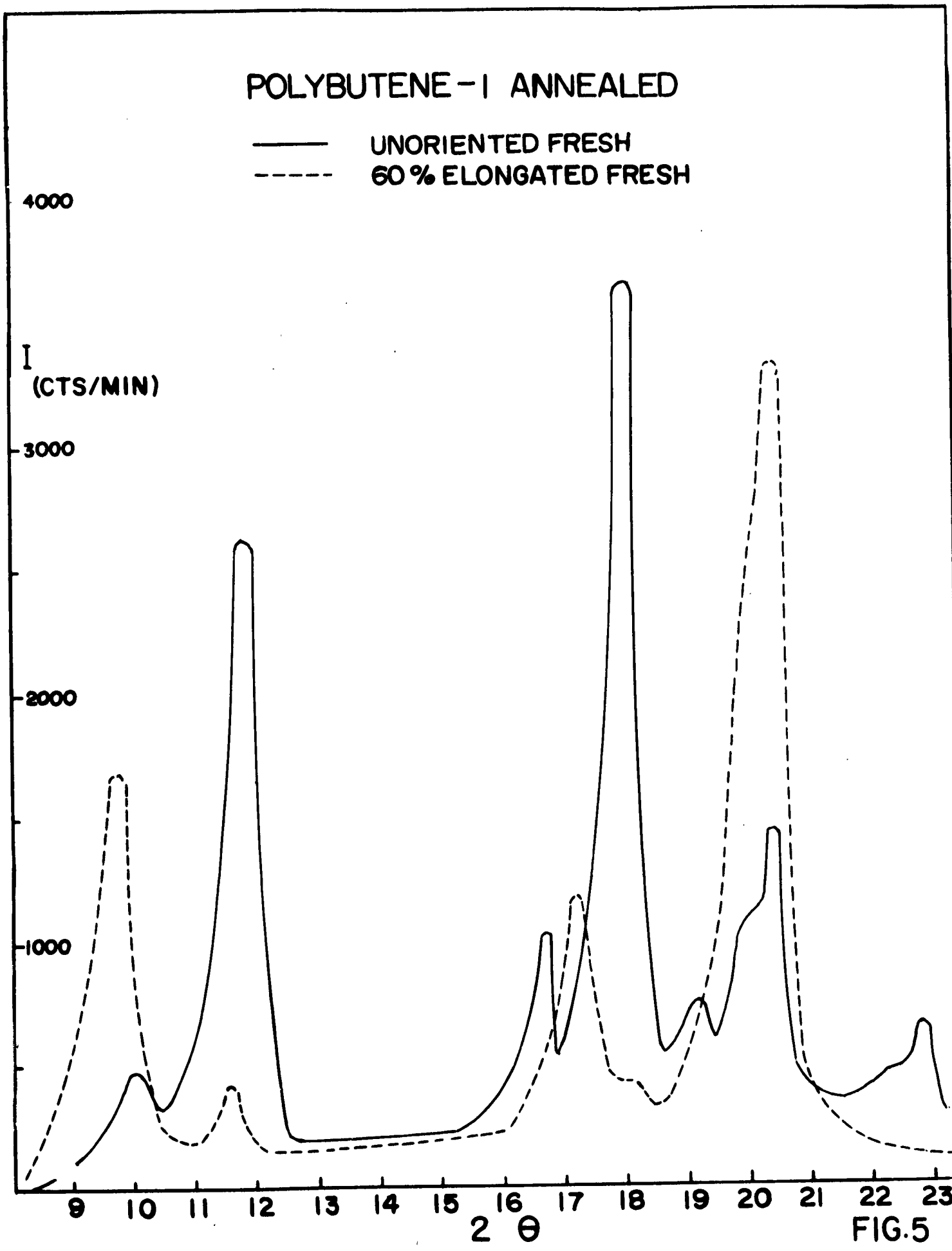

POLYBUTENE-1 ANNEALED
UNORIENTED FRESH
60% ELONGATED FRESH
4000
I
(CTS/MIN)
3000
2000
1000
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
2 θ

FIG.5

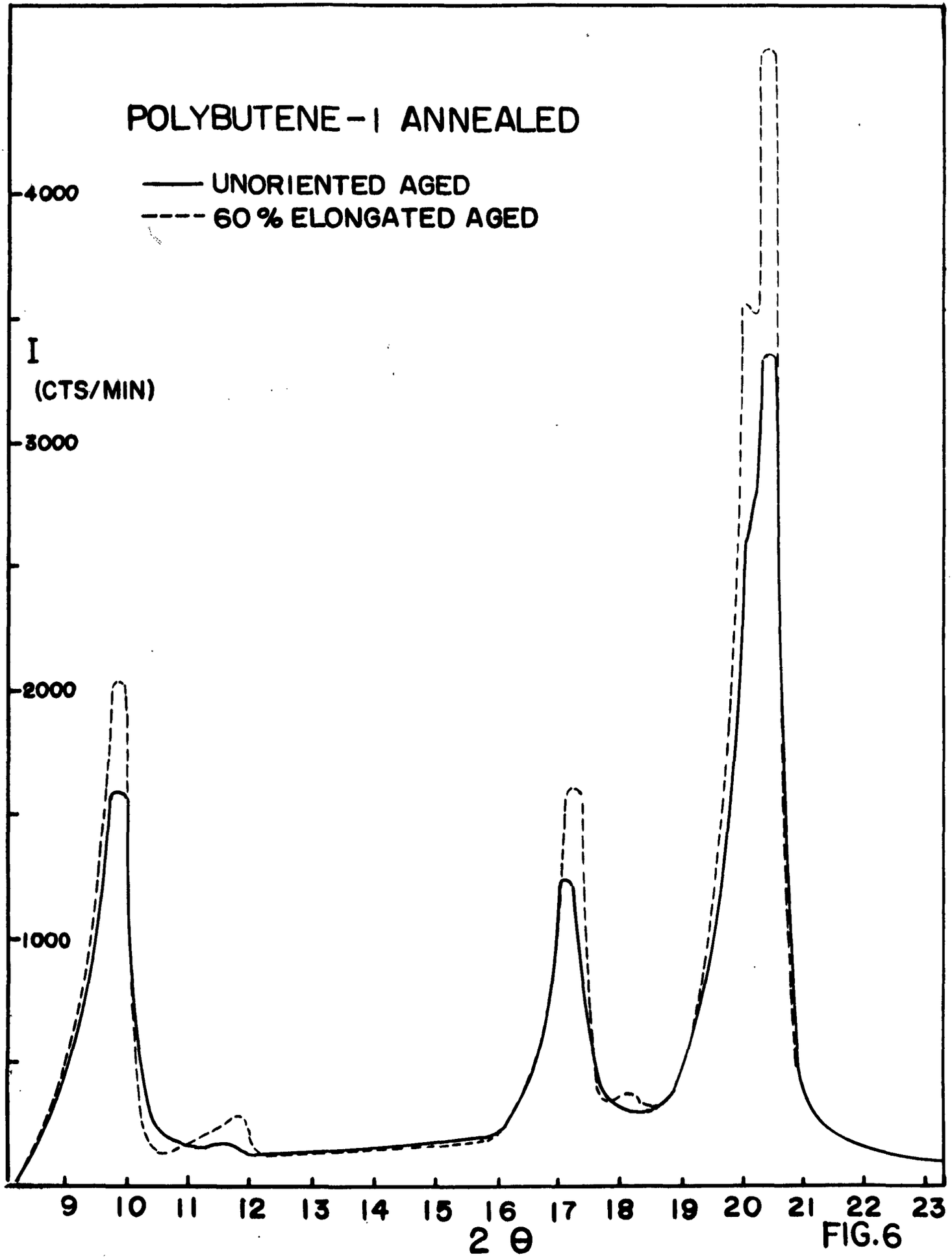
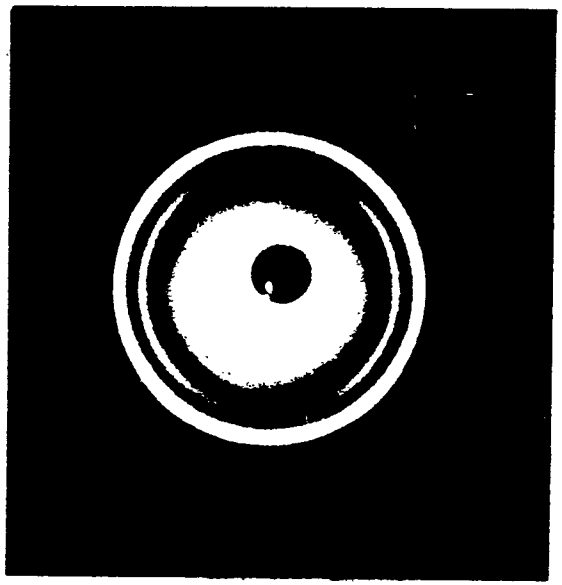
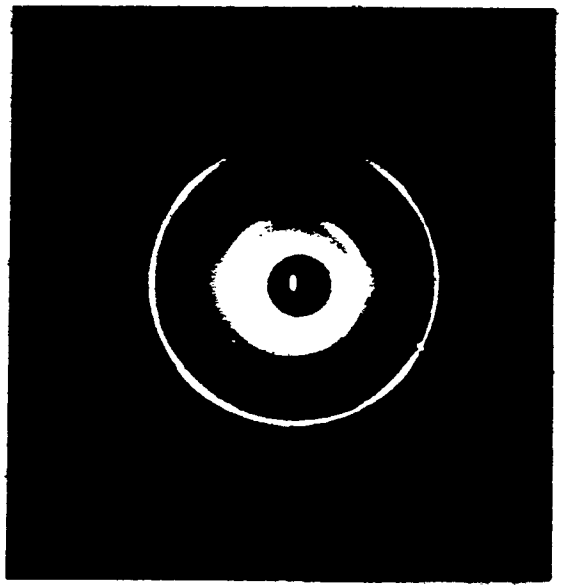

POLYBUTENE-1 ANNEALED
UNORIENTED AGED
60% ELONGATED AGED
4000
I
(CTS/MIN)
3000
2000
1000
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
2θ

FIG.6

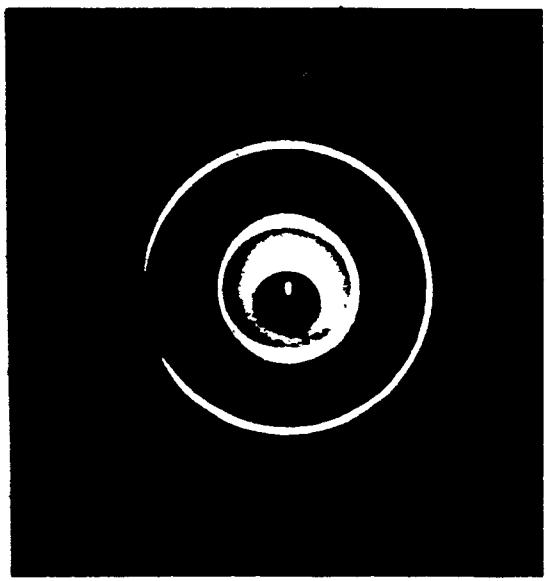
0 % (FRESH)



100 %

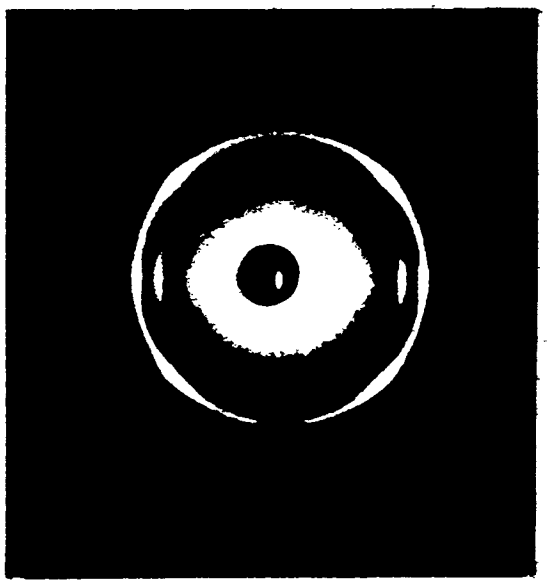


140 %

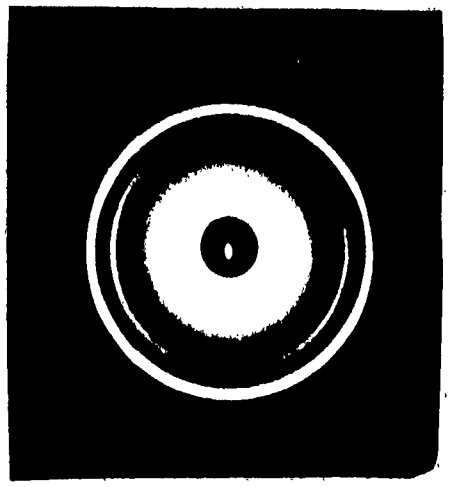


0 % (AGED), 7DAYS

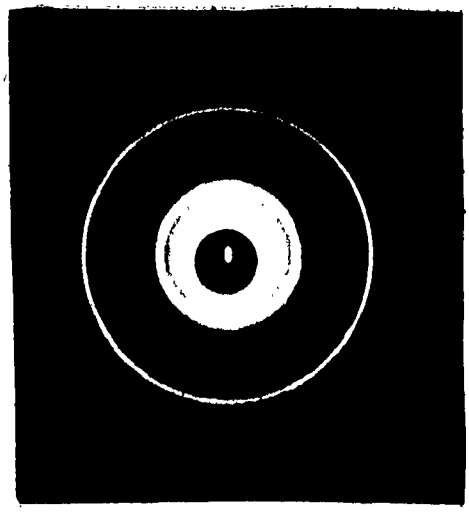
Fig. 7



200 %



0 %



50 %

Fig. 8

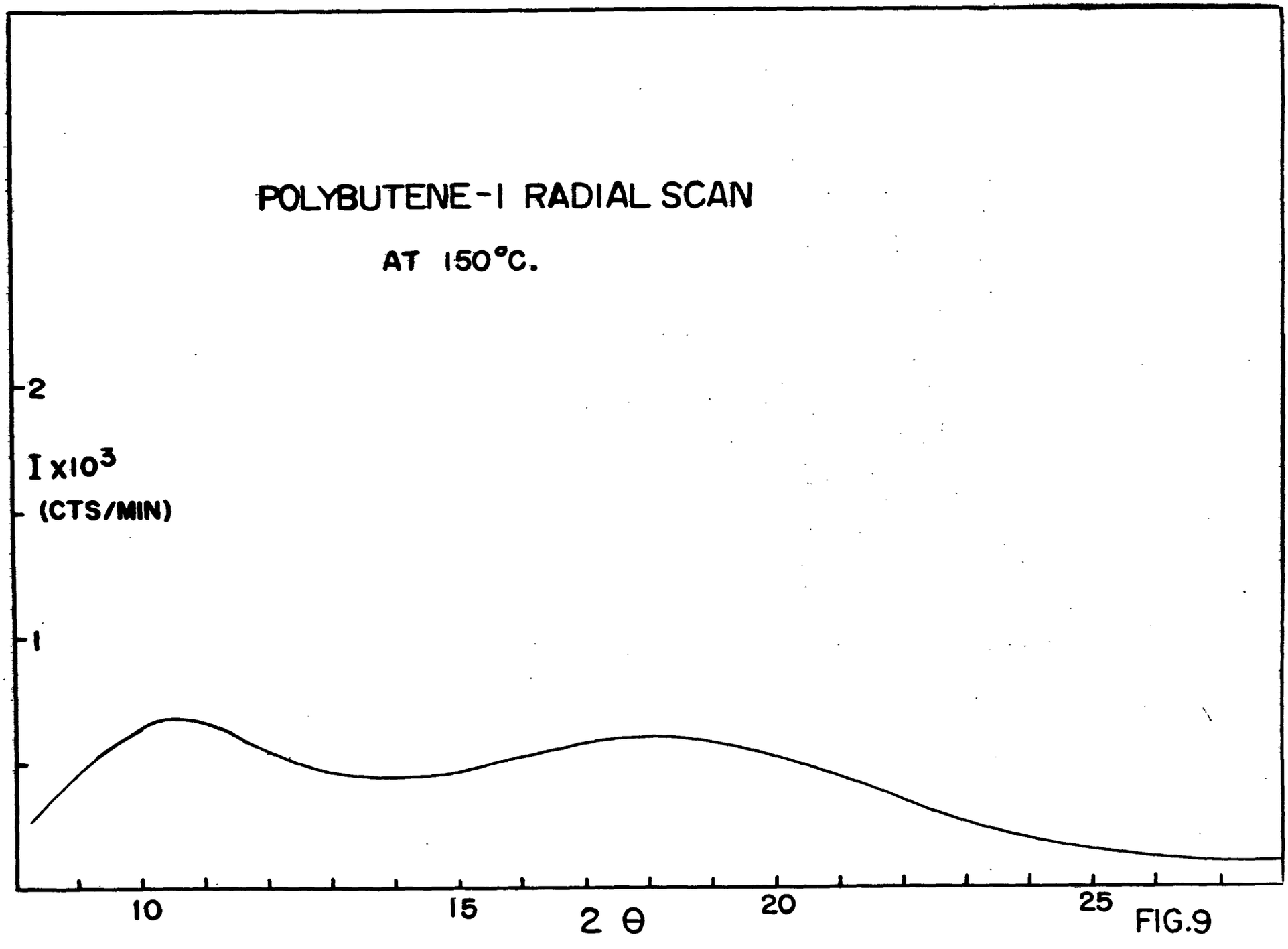

POLYBUTENE-1 RADIAL SCAN
AT 150°C.
2
I x10³
(CTS/MIN)
1
10
15
2 θ
20
25

FIG.9

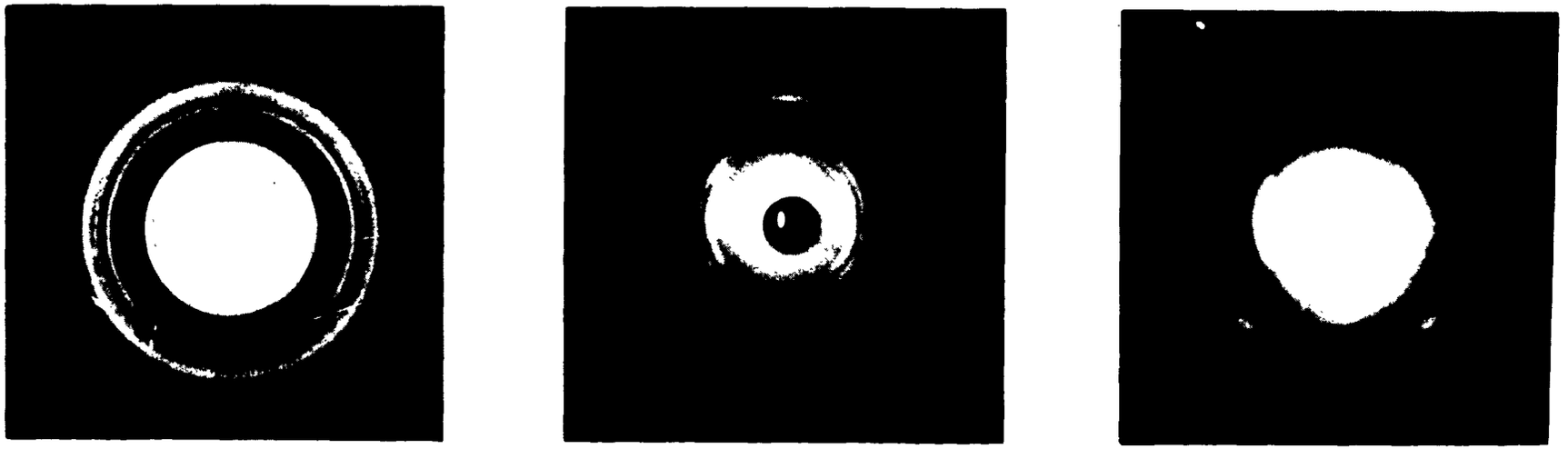
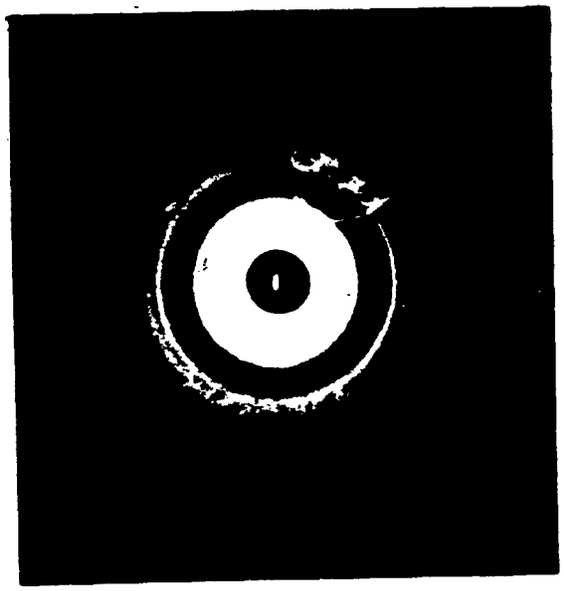
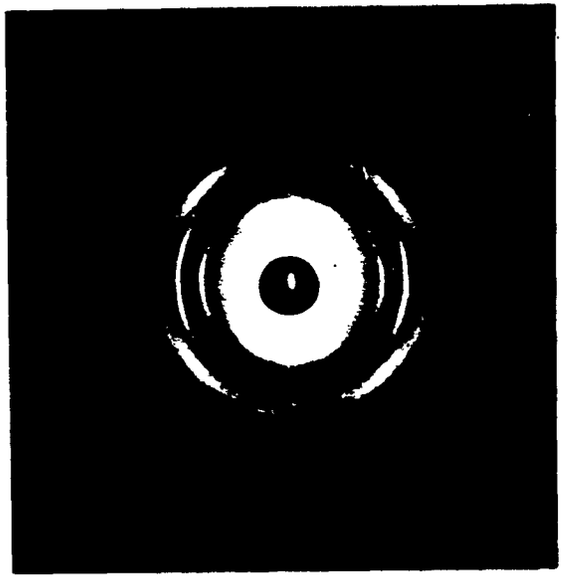


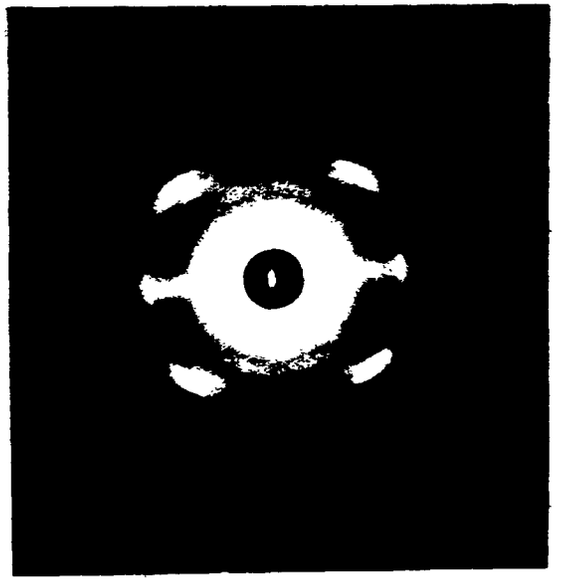
Fig. 10. X-ray diffraction photographs of annealed polypentene-1 at various percentages of elongation.



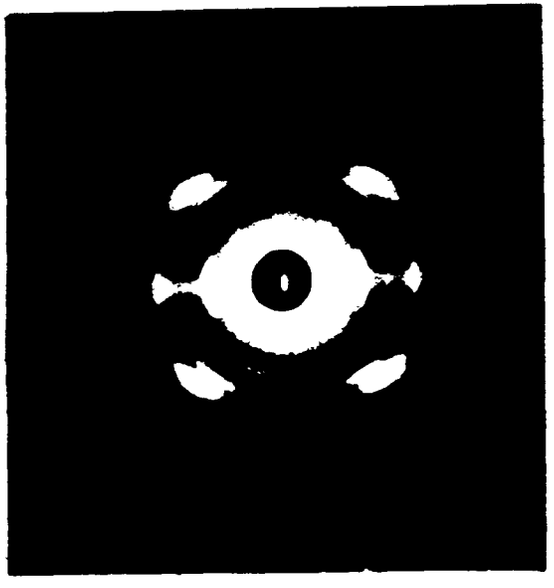
0 %



200 %



300 %



350 %

Fig. 11

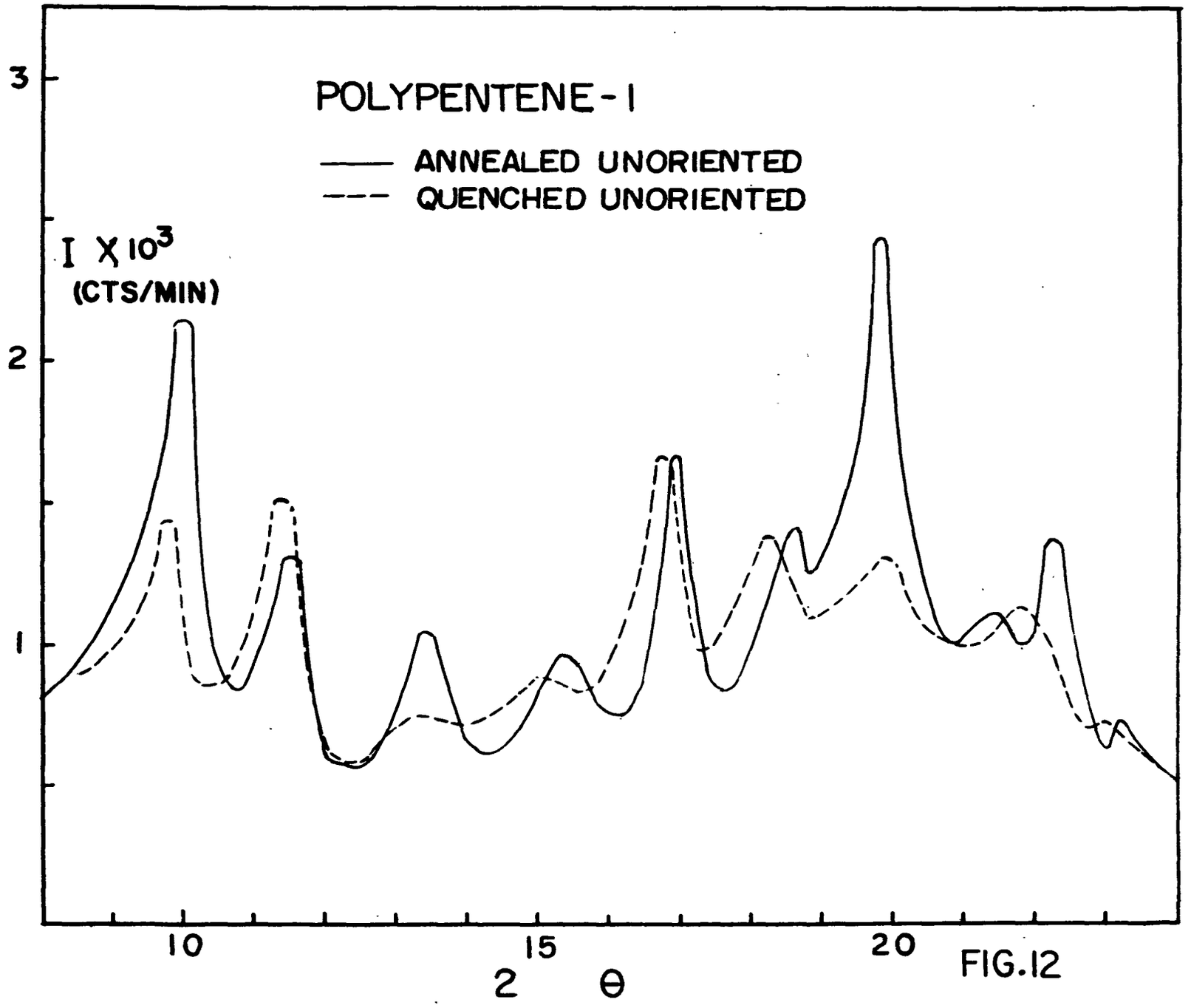

POLYPENTENE-I
ANNEALED UNORIENTED
QUENCHED UNORIENTED
I X 10³
(CTS/MIN)
3
2
1
10
15
20
2 θ

FIG.12

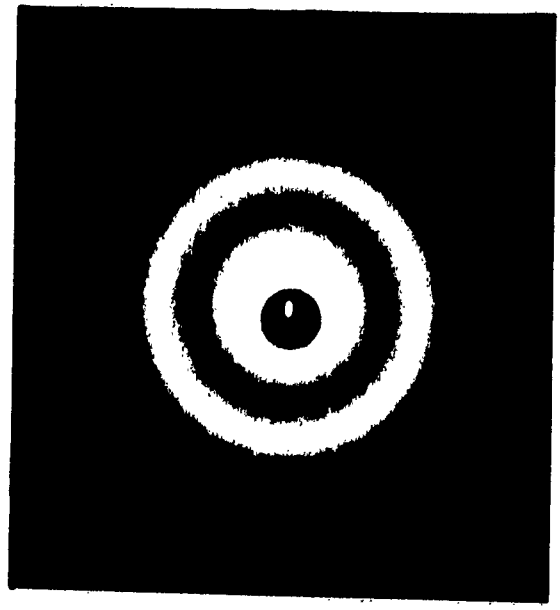


Fig. 13